Laboratory Demonstration of Capability Procedure

An environmental testing laboratory wishing to submit Wastewater Laboratory Certification compliance data to Kentucky Division of Water must use an Environmental Protection Agency (EPA) approved wastewater method specified in 40 CFR Part 136.3 in accordance with the Commonwealth of Kentucky Wastewater Laboratory Certification Manual; June 2013 (WWCM) and 401 KAR 5:320. The laboratory must also demonstrate the capability to report the results of wastewater analyses at or below the required reporting limit (RRL) as established by either the Commonwealth of Kentucky or the EPA.

To effectively demonstrate method capability the laboratory must: 1) perform an initial demonstration of capability (IDC); 2) perform an on-going demonstration of capability (ODC) annually; 3) perform a method detection limit study (MDL) annually using 40 CFR Part 136 Appendix B guideline; and 4) perform a reporting limit standard (RLS) in accordance with WWCM Chapter III; Section 7.1.3.

Initial Demonstration of Capability / On-going Demonstration of Capability - IDC / ODC

An IDC and ODC are used to demonstrate that the laboratory and analyst are capable of performing analysis with acceptable precision, accuracy, sensitivity and specificity pertaining to that particular method. This is done by analyzing four (4) mid-range concentration laboratory fortified blanks (LFB) on the same or different day, and then calculating the percent recovery for each. The percent recovery is used to verify that all of the following criteria are met:

- each of the four IDCs (or ODCs) are within 80 to 120% of the mean value;
- the calculated percent relative standard deviation (%RSD) is at or below 15% (WWCM);
- Other limits may apply as specified in the method or individually approved by DOW based on method performance.

An IDC must be performed initially by each analyst on each instrument used to analyze compliance/permit samples.

An ODC must be performed annually by the primary analyst/technician and at least once per five year audit cycle for all backup analysts.

The Percent Relative Standard Deviation (%RSD) shall be calculated as follows:

$$\%RSD = \frac{s}{\bar{x}} \text{ x } 100\%$$

where s = standard deviation (n-1)

$\bar{x}$ = mean of 4 replicates

Method Detection Limit - MDL

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the target analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing the target analyte and is established using the EPA technique specified in 40 CFR Part 136 Appendix B. Laboratories that do not analyze an MDL per each instrument shall demonstrate that the Minimum Reporting Limit (MRL) is achievable on all instruments that the MDL study is applied. A summary of the procedure is as follows:

- Analyze seven (7) laboratory fortified blanks (LFB) over two (2) to three (3) non-consecutive days. If the spike level exceeds ten (10) times the calculated MDL, then the MDL determination must be performed again using an appropriate calculated spike concentration;
- Calculate the variance (S^2) and standard deviation (S) of the replicate measurements;
- Compute the MDL using the following equation: MDL = 3.143 * S for seven replicates;
- The calculated MDL must be less than the required reporting limit.
- Your laboratory's MRL must be greater than the calculated MDL and less than or equal to the required reporting limit.

Calculate the MDL using the instructions provided below:

Calculate S^2 and S:	$S^2 = \frac{1}{n-1}\left[\sum_{i=1}^{n} x_i^2 - \frac{\left(\sum_{i=1}^{n} X_i\right)^2}{n}\right] \quad S = \left(S^2\right)^{\frac{1}{2}}$
Calculate MDL:	MDL = (S) x (3.143) for 7 replicates

Required Reporting Limit Standard - RLS

In order to demonstrate the laboratory's capability to report down to the required reporting limit, the laboratory shall analyze a known standard at or below their minimum reporting limit (MRL). The reporting limit standard (RLS) must be analyzed as either a low concentration calibration standard or as a stand alone verification standard.

If the RLS is used as a low concentration calibration standard it must also be used to determine the acceptance of the calibration curve. The RLS must meet the acceptance criteria set by the laboratory. The lowest value of the calibration standard cannot be ignored or not considered during any future verification of the calibration curve – unless the MRL is raised to the concentration of the next calibration standard.

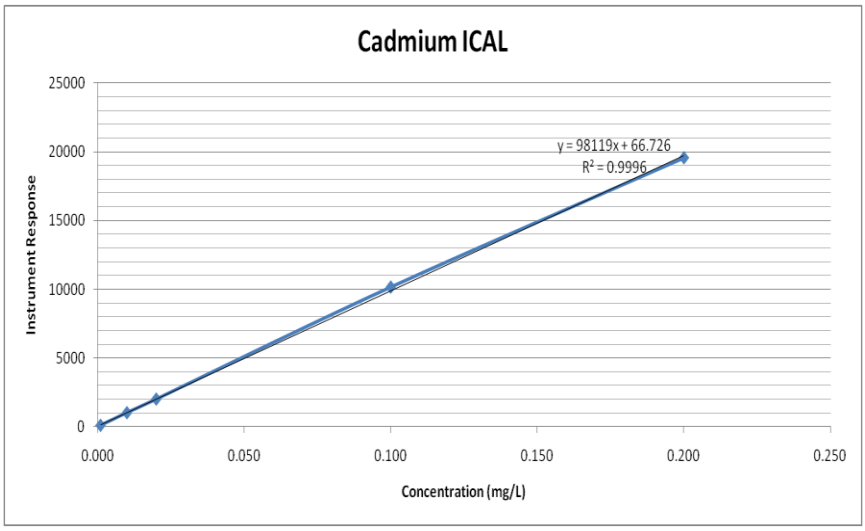
If the RLS is used as a stand alone standard it shall meet the acceptance criteria set by the laboratory. The WWCM requires that the RLS is analyzed with each new calibration curve but at least quarterly for all methods.

Example: Linear calibration curve (linear regression) is calculated as follows:

1. Plot all x,y pairs;
2. y = mx + b where: m=slope
   x = concentration
   y = instrument response

An example of the RLS used as the lowest concentration calibration standard is shown below:

Contaminant	RRL (mg/L)	Date of Analysis	Graph Axis	STD#1	STD#2	STD#3	STD#4	STD#5
Cadmium	0.001	6/17/2011	Conc (x)	0.001	0.010	0.020	0.100	0.200
			Response (y)	91	1010	2000	10150	19560



In the case above, the following example provides an example for reporting cadmium results to DOW:

Assume: Cadmium MDL = 0.0001 mg/L
From above: Cadmium MRL = 0.001 mg/L

- For a result not detected at or above the MRL, use:

  Cadmium <0.001 mg/L

- For a result of 0.0008 mg/L that is detected below the MRL but above the MDL, use:

  Cadmium 0.0008 J mg/L (J is used as a flag for estimated result)

- For a result that is not detected at or above the MDL, use:

  Cadmium BDL (defined as "below detection limit")
  Cadmium B (required for a Kentucky DMR report)

NOTE: In this instance, the MRL is equal to the required reporting limit and also equal to the lowest calibration standard concentration.

Laboratory Submission to DOW - Initial

The DOW Wastewater Laboratory Certification Program requires that laboratories submit the following results of the Initial Demonstration of Capability to DOW in accordance with 401 KAR 5:320 Kentucky Wastewater Laboratory Certification Program Application; June 2013. The submission must include:

1. EPA reference method, including version OR Standard Methods reference method and year approved (ex. SM 2340 C – 1997);
2. Date of analysis;
3. Analyst's name performing the analysis;
4. Initial Demonstration of Capability (IDC) results showing the spiked concentration, units and percent recoveries of all four (4) fortified samples; the calculated mean of the percent recoveries; the calculated percent relative standard deviation (%RSD);
5. Method Detection Limit Study (MDL) results showing the spiked concentration, units and the concentrations found for each of the seven (7) replicates; the calculated variance; and the calculated MDL. Laboratories must ensure that the spike concentration is less than 10 times the calculated MDL.

Laboratory Submission to DOW - Ongoing

The DOW Wastewater Laboratory Certification Program requests that laboratories submit the following results of the Ongoing Demonstration of Capability to DOW. The annual submission must include:

1. EPA reference method, including version OR Standard Methods method and edition;
2. Date of analysis;
3. Analyst's name performing the analysis;
4. Ongoing Demonstration of Capability (ODC) results showing the spiked concentration, units and percent recoveries of all four (4) fortified samples; the calculated mean of the percent recoveries; the calculated percent relative standard deviation (%RSD);
5. Annual Method Detection Limit Study (MDL) results showing the spiked concentration, units and the concentrations found for each of the seven (7) replicates; the calculated variance; and the calculated MDL. Laboratories must ensure that the spike concentration is less than 10 times the calculated MDL.

DOW may, at any time, request that laboratories submit verification of the Reporting Limit Standard (RLS) in accordance with the Wastewater Lab Certification Program Manual. The submission for verification of Initial Calibration Curve (ICAL) or Continuing Calibration Verification (CCV) includes results and raw data showing that a valid standard is at or below the laboratory's minimum reporting limit (MRL) or the compliance/permit required reporting limit

Summary of Demonstration of Capability Requirements, Acceptance Criteria and Frequency

Demonstration	Parameter	Requirement	Frequency
IDC/ODC	IDC Replicates (4 mid-range LCS)	• Each shall be within 80 to 120% of the mean value; • %RSD shall be $\leq$ 15%.	Initial and Annual
MDL	7 Replicates	• Replicates analyzed over 2 to 3 non-consecutive days; • Calculated MDL shall be less than the MRL; • Spike concentration shall be less than 10 times the calculated MDL.	Initial and Annual
RLS	Verification Standard	• Concentration shall be $\leq$ MRL.	Performed with each calibration but at least quarterly

Initial/Ongoing Demonstration of Capabilities (IDC/ODC)

KENTUCKY DEPARTMENT FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER
200 FAIR OAKS LANE; 4TH FLOOR
FRANKFORT, KY 40601

IDC/ODC Results

Laboratory Name:	
Analysis Date Range:	
Analyst:	
Instrument ID:	

Contaminant	RRL[1]	Units	Spike Conc	#1	#2	#3	#4	Mean	% Rec[2] #1	% Rec #2	% Rec #3	% Rec #4	%RSD	-20% Limit	+20% Limit
													-		
													-		
													-		
													-		
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													-		
													-		

1. RRL = Required Reporting Limit
2. % Rec = Percent Recovery [(known / expected)*100%]

Minimum Detection Limit Study (MDL)

KENTUCKY DEPARTMENT FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER
200 FAIR OAKS LANE; 4TH FLOOR
FRANKFORT, KY 40601

Minimum Detection Limit (MDL) Results

Laboratory Name:	
Analyst:	
Instrument ID:	

					Date	Date	Date	Date	Date	Date	Date			
Analysis date of each replicate >>														
Contaminant	**RRL[1]**	**Units**	**Est. MDL**	**Spike Conc**	**#1**	**#2**	**#3**	**#4**	**#5**	**#6**	**#7**	**Std. Dev.**	**MDL[2]**	**MRL[3]**
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1. RRL = Required Reporting Limit
2. MDL = Minimum Detection Limit
3. MRL = Minimum Reporting Level

Reporting Limit Standard (RLS)
KENTUCKY DEPARTMENT FOR ENVIRONMENTAL PROTECTION
DIVISION OF WATER
200 FAIR OAKS LANE; 4TH FLOOR
FRANKFORT, KY 40601

ICAL with Reporting Limit Standard

Laboratory Name:	

Contaminant	RRL1	Units	Date of Analysis	Graph Axis	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
				Concentration (x)										
				Instr. Response (y)										
				Concentration (x)										
				Instr. Response (y)										
				Concentration (x)										
				Instr. Response (y)										
				Concentration (x)										
				Instr. Response (y)										
				Concentration (x)										
				Instr. Response (y)										

ICAL Statistics

The % Recovery was calculated using a pre-programmed curve

Contaminant	Analyst	Instrument ID	Number of Points	Correlation Coefficient (R2)	Y – intercept	Slope (m)	Percent Recovery (%REC) of RLS		Acceptable? (according to QAP)
							-	-	
							-	-	
							-	-	
							-	-	
							-	-	

RRL = Required Reporting Limit
ICAL = Initial Calibration

DEFINITIONS

Confirmation: verification of the presence of a component through the use of an analytical technique based on a different scientific principle from the original method (e.g., second column, alternate wavelength or detector, etc.).

Continuing Calibration Check Standard (CCC): is a standard containing one or more of the target analytes that is prepared from the same standards used to calibrate the instrument. This standard is used to verify the calibration curve at the beginning of each analytical sequence. It may also be analyzed throughout and at the end of the sequence. The concentration of continuing standards may be varied, when prescribed by the reference method, so that the range of the calibration curve is verified on a regular basis.

Continuing Calibration Verification (CCV): see Continuing Calibration Check Standard (CCC).

Compliance sample: any sample submitted to DOW under a permitting program to fulfill requirements of a permit. Results of sample should usually meet a defined standard as stated in the permit.

DOW: Kentucky's Division of Water.

EPA: Environmental Protection Agency.

Initial Calibration Check Standard (ICCS): see Reporting Limit Standard (RLS).

Initial Calibration Standard (ICAL): a solution prepared from the primary dilution standard solution or stock standard solutions and diluted as needed to prepare an initial calibration curve.

Initial Calibration Verification Standard (ICV): see Continuing Calibration Check Standard (CCC).

Laboratory Fortified Blank (LFB): (Spike) is an aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

Method Detection Limit (MDL): the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The MDL is determined from analysis of a sample in a given matrix containing this analyte. See 40 CFR 136 App. B.

Minimum Reporting Limit (MRL): the lowest concentration that is reported by the laboratory.

Permit effluent sample: a sample submitted under a permitting program that relates directly to a permitted discharge.

Reporting Limit Standard (RLS): is a standard that is analyzed each day to evaluate instrument performance at or below the minimum reporting limit.